

Dynamic Phase Transitions in PVT Systems*

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The main objective of this article are two-fold. First, we introduce some general principles on phase transition dynamics, including a new dynamic transition classification scheme, and a Ginzburg-Landau theory for modeling equilibrium phase transitions. Second, apply the general principles and the recently developed dynamic transition theory to study dynamic phase transitions of PVT systems. In particular, we establish a new time-dependent Ginzburg-Landau model, whose dynamic transition analysis is carried out. It is worth pointing out that the new dynamic transition theory, along with the dynamic classification scheme and new time-dependent Ginzburg Landau models for equilibrium phase transitions can be used in other phase transition problems, including e.g. the ferromagnetism and superfluidity, which will be reported elsewhere. In addition, the analysis for the PVT system in this article leads to a few physical predications, which are otherwise unclear from the physical point of view.

PACS numbers:

I. INTRODUCTION

The main objectives of this article are

- 1) to introduce a new dynamic phase transition classification scheme for nonlinear systems,
- 2) to present a new time-dependent Ginzburg-Landau model for general equilibrium phase transitions, and
- 3) to study the dynamic phase transitions for PVT systems.

As we know, there are several classification schemes for phase transitions. The one used most often is the classical Ehrenfest classification scheme, which is based on the order of differentiability of the energy functional. The new dynamic phase transition classification scheme we propose here is based on the dynamic transition theory developed recently by the authors [1, 2], which has been used to study numerous problems in sciences and engineering, including in particular problems in classical and geophysical fluid dynamics, biology and chemistry, and phase transitions. The new scheme introduced in this article classifies phase transitions into three categories: Type-I, Type-II and Type-III, corresponding respectively to the continuous, the jump and mixed transitions in the mathematical dynamic transition theory.

We shall see from the applications to PVT systems that this new classification scheme is more transparent. In addition, it can be used to identify high-order (in the

Ehrenfest sense) transitions, which are usually hard to derive both theoretically and experimentally.

Second, based on the le Châtelier principle and some general characteristics of pseudo-gradient systems, we introduce a general principle, leading to a unified approach to derive Ginzburg-Landau type of time-dependent models for equilibrium phase transitions. In view of this new dynamic modeling and the dynamic transition theory, we shall see that the states after transition often include not only equilibria, but also some transient states, which are physically important as well.

Third, with the aforementioned principles in our disposal, we derive a new dynamic model for PVT system, whose dynamic transition can be explicitly obtained, leading to some specific physical predictions.

As we know, a *PVT* system is a system composed of one type of molecules, and the interaction between molecules is governed by the van der Waals law. The molecules generally have a repulsive core and a short-range attraction region outside the core. Such systems have a number of phases: gas, liquid and solid, and a solid can appear in a few phases. The most typical example of a *PVT* system is water. In general, the phase transitions of *PVT* systems mainly refer to the gas-liquid, gas-solid and liquid-solid phase transitions. These transitions are all first order in the Ehrenfest sense (i.e., discontinuous) and are accompanied by a latent heat and a change in density.

A *PT*-phase diagram of a typical *PVT* system is schematically illustrated by Figure 1, where point *A* is the triple point at which the gas, liquid, and solid phases can coexist. Point *C* is the Andrews critical point at which the gas-liquid coexistence curve terminates [3]. The fact that the gas-liquid coexistence curve has a critical point means that we can go continuously from a gaseous state to a liquid state without ever meeting an

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observable phase transition, if we choose the right path. The critical point in the liquid-solid coexistence curve has never been observed. It implies that we must go through a first-order phase transition in going from the liquid to the solid state.

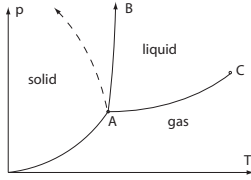


FIG. 1: Coexistence curves of a typical PVT system: A is the triple point, C is the critical point, and the dashed curve is a melting line with negative slope.

The phase diagram in the PV -plane is given by Figure 2, where the dashed curves represent lines of constant temperature. In the region of coexistence of phases, the isotherms (dashed lines) are always flat, indicating that in these regions the change in volume (density) occurs for constant pressure p and temperature T .

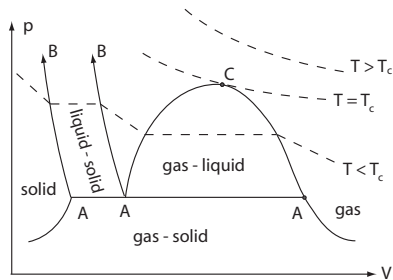


FIG. 2: PV -phase diagram, the dashed line represent isotherms.

One of the main objectives of this article is to study the dynamic phase transitions beyond the Andrews point C , and to make some physical predictions.

For this purpose, first, by both mathematical and physical considerations, a proper form of the Gibbs free energy functional is given, and then the time-dependent Ginzburg-Landau type of model for PVT systems is derived naturally using the general principle as mentioned above.

Then, using the dynamical transition theory, we derive a system of critical parameter equations to determine the Andrews point $C = (T_C, p_C)$ given by (V.6). Then we show that the gas-liquid transition can be either first-order, second order or third order, as demonstrated in Physical Conclusion V.1, if we go from a gas to a liquid by a path without passing through the gas-liquid coexistence curve.

In addition, in the gas-solid and liquid-solid transitions, there also exist metastable states. For the gas-solid case, the metastable states correspond to the superheated solid and supercooled liquid, and for the liquid-solid case, the metastable states correspond to the superheated solid and supercooled liquid; see Physical Conclusion V.2.

This article is organized as follows. The new dynamic classification scheme and the Ginzburg-Landau model for equilibrium phase transitions are given in Section II. Section III introduces a time-dependent model for PVT systems, which is analyzed in Section IV. Section V provides physical consequences of the analysis and some new physical predictions. The abstract dynamical transition theory is recapitulated in the Appendix A for convenience.

II. GENERAL PRINCIPLES OF PHASE TRANSITION DYNAMICS

In this section, we introduce a new phase dynamic transition classification scheme to classify phase transitions into three categories: Type-I, Type-II and Type-III, corresponding mathematically continuous, jump mixed transitions, respectively.

Then a new time-dependent Ginzburg-Landau theory for modeling equilibrium phase transitions in statistical physics is derived based on the le Châtelier principle and some mathematical insights on pseudo-gradient systems.

A. Dynamic Classification Scheme

In sciences, nonlinear dissipative systems are generally governed by differential equations, which can be expressed in the following abstract form

$$\begin{aligned} \frac{du}{dt} &= L_\lambda u + G(u, \lambda), \\ u(0) &= \varphi, \end{aligned} \quad (\text{II.1})$$

where $u : [0, \infty) \rightarrow X$ is the unknown function, $\lambda \in \mathbb{R}^N$ ($N \geq 1$) is the control parameter, X and X_1 are two Banach spaces with $X_1 \subset X$ being a dense and compact inclusion, $L_\lambda = -A + B_\lambda$ and $G(\cdot, \lambda) : X_1 \rightarrow X$ are C^r ($r \geq 0$) mappings depending continuously on λ , $L_\lambda : X_1 \rightarrow X$ is a sectorial operator, and

$$\begin{aligned} A : X_1 &\rightarrow X \quad \text{a linear homeomorphism,} \\ B_\lambda : X_1 &\rightarrow X \quad \text{a linear compact operator.} \end{aligned} \quad (\text{II.2})$$

In following, we introduce some basic and universal concepts in nonlinear sciences.

First, a state of the system (II.1) at λ is usually referred to as a compact invariant set Σ_λ . In many applications, Σ_λ is a singular point or a periodic orbit. A state Σ_λ of (II.1) is stable if Σ_λ is an attractor, otherwise Σ_λ is called unstable.

Second, we say that the system (II.1) has a phase transition from a state Σ_λ at $\lambda = \lambda_0$ if Σ_λ is stable on $\lambda < \lambda_0$

(or on $\lambda > \lambda_0$) and is unstable on $\lambda > \lambda_0$ (or on $\lambda < \lambda_0$). The critical parameter λ_0 is called a critical point. In other words, the phase transition corresponds to an exchange of stable states.

The concept of phase transition originates from the statistical physics and thermodynamics. In physics and chemistry, "phase" means the homogeneous part in a heterogeneous system. However, here the so called phase means the stable state in the systems of nonlinear sciences including physics, chemistry, biology, ecology, economics, fluid dynamics and geophysical fluid dynamics, etc. Hence, here the content of phase transition has been endowed with more general significance. In fact, the phase transition dynamics introduced here can be applied to a wide variety of topics involving the universal critical phenomena of state changes in nature in a unified mathematical viewpoint and manner.

Third, if the system (II.1) possesses the gradient-type structure, then the phase transitions are called equilibrium phase transition; otherwise they are called the non-equilibrium phase transitions.

Fourth, classically, there are several ways to classify phase transitions. The one most used is the Ehrenfest classification scheme, which groups phase transitions based on the degree of non-analyticity involved. First order phase transitions are also called discontinuous, and higher order phase transitions ($n > 1$) are called continuous.

Here we introduce the following notion of dynamic classification scheme:

Definition II.1 Let $\lambda_0 \in \mathbb{R}^N$ be a critical point of (II.1), and (II.1) undergo a transition from state Σ_λ^1 to Σ_λ^2 . There are three types of phase transitions for (II.1) at $\lambda = \lambda_0$, depending on their dynamic properties: continuous, jump, and mixed as given in Theorem A.1, which are called Type-I, Type-II and Type-III respectively.

The main characteristics of Type-II phase transitions is that there is a gap between Σ_λ^1 and Σ_λ^2 at the critical point λ_0 . In thermodynamics, the metastable states correspond in general to the super-heated or super-cooled states, which have been found in many physical phenomena. In particular, Type-II phase transitions are always accompanied with the latent heat to occur.

In a Type-I phase transition, two states Σ_λ^1 and Σ_λ^2 meet at λ_0 , i.e., the system undergoes a continuous transition from Σ_λ^1 to Σ_λ^2 .

In a Type-III phase transition, there are at least two different stable states Σ_λ^2 and Σ_λ^3 at λ_0 , and system undergoes a continuous transition to Σ_λ^2 or a jump transition to Σ_λ^3 , depending on the fluctuations.

It is clear that a Type-II phase transition of gradient-type systems must be discontinuous or the zero order because there is a gap between Σ_λ^1 and Σ_λ^j ($2 \leq j \leq K$). For a Type-I phase transition, the energy is continuous, and consequently, it is an n -th order transition in the Ehrenfest sense for some $n \geq 2$. A Type-III phase transition is indefinite, for the transition from Σ_λ^1 to Σ_λ^2 it

may be continuous, i.e., $dF^-/d\lambda = dF_2^+/d\lambda$, and for the transitions from Σ_λ^1 to Σ_λ^3 it may be discontinuous: $dF^-/d\lambda \neq dF_3^+/d\lambda$ at $\lambda = \lambda_0$.

Finally, we recall the physical meaning of the derivatives of $F(u, \lambda)$ on λ in statistical physics. In thermodynamics, the parameter λ generally stands for temperature T and pressure p

$$\lambda = (T, p).$$

The energy functional $F(u, T, p)$ is the thermodynamic potential, and u is the order parameter. The first order derivatives are

$$\begin{aligned} -\frac{\partial F}{\partial T} &= S && \text{the entropy,} \\ \frac{\partial F}{\partial p} &= V && \text{the phase volume,} \end{aligned}$$

and the second order derivatives are

$$\begin{aligned} -T \frac{\partial^2 F}{\partial T^2} &= C_p && \text{the heat capacity in constant pressure,} \\ -\frac{1}{V} \frac{\partial^2 F}{\partial p^2} &= \kappa && \text{the compression coefficient,} \\ \frac{1}{V} \frac{\partial^2 F}{\partial T \partial p} &= \alpha && \text{the thermal expansion coefficient,} \end{aligned}$$

for the PVT system.

Thus, for the first order phase transition, the discontinuity of $\partial F/\partial p$ at critical point $\lambda_0 = (T_0, p_0)$ implies the discontinuity of phase volume:

$$\Delta V = V^2 - V^1 = \frac{\partial F^+}{\partial p} - \frac{\partial F^-}{\partial p}, \quad (\text{II.3})$$

and the discontinuity of $\partial F/\partial T$ implies that there is a gap between both phase entropies:

$$\Delta S = S^2 - S^1 = -\frac{\partial F^+}{\partial T} + \frac{\partial F^-}{\partial T} \quad (\text{II.4})$$

Physically, ΔS is a non-measurable quantity, hence, we always use latent heat $\Delta H = T\Delta S$ to determine the first order phase transition, and ΔH stand for the absorbing heat for transition from phase Σ_λ^1 to phase Σ_λ^2 . In the two phase coexistence situation, ΔH and ΔV are related by the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}.$$

For second order phase transitions the variance of heat capacity (or specific heat), compression coefficient, and the thermal expansion coefficient at critical value are important static properties in equilibrium phase transition, which are measurable physical quantities.

B. New Ginzburg-Landau Models for Equilibrium Phase Transitions

In this subsection, we introduce the time-dependent Ginzburg-Landau model for equilibrium phase transitions.

We start with thermodynamic potentials and the Ginzburg-Landau free energy. As we know, four thermodynamic potentials—internal energy, the enthalpy, the Helmholtz free energy and the Gibbs free energy—are useful in the chemical thermodynamics of reactions and non-cyclic processes.

Consider a thermal system, its order parameter u changes in $\Omega \subset \mathbb{R}^n$ ($1 \leq n \leq 3$). In this situation, the free energy of this system is of the form

$$\mathcal{H}(u, \lambda) = \mathcal{H}_0 + \int_{\Omega} \left[\frac{1}{2} \sum_{i=1}^m \mu_i |\nabla u_i|^2 + g(u, \nabla u, \lambda) \right] dx \quad (\text{II.5})$$

where $N \geq 3$ is an integer, $u = (u_1, \dots, u_m)$, $\mu_i = \mu_i(\lambda) > 0$, and $g(u, \nabla u, \lambda)$ is a C^r ($r \geq 2$) function of $(u, \nabla u)$ with the Taylor expansion

$$g(u, \nabla u, \lambda) = \sum \alpha_{ijk} u_i D_j u_k + \sum_{|I|=1}^N \alpha_I u^I + o(|u|^N) - fX, \quad (\text{II.6})$$

where $I = (i_1, \dots, i_m)$, $i_k \geq 0$ are integer, $|I| = \sum_{k=1}^m i_k$, the coefficients α_{ijk} and α_I continuously depend on λ , which are determined by the concrete physical problem, $u^I = u_1^{i_1} \dots u_m^{i_m}$ and fX the generalized work.

Thus, the study of thermal equilibrium phase transition for the static situation is referred to the steady state bifurcation of the system of elliptic equations

$$\begin{aligned} \frac{\delta}{\delta u} \mathcal{H}(u, \lambda) &= 0, \\ \frac{\partial u}{\partial n} \Big|_{\partial\Omega} &= 0, \quad (\text{or } u|_{\partial\Omega} = 0), \end{aligned}$$

where $\delta/\delta u$ is the variational derivative.

A thermal system is controlled by some parameter λ . When λ is for from the critical point λ_0 the system lies on a stable equilibrium state Σ_1 , and when λ reaches or exceeds λ_0 the state Σ_1 becomes unstable, and meanwhile the system will undergo a transition from Σ_1 to another stable state Σ_2 . The basic principle is that there often exists fluctuations in the system leading to a deviation from the equilibrium states, and the phase transition process is a dynamical behavior, which should be described by a time-dependent equation.

To derive a general time-dependent model, first we recall that the classical le Châtelier principle amounts to saying that for a stable equilibrium state of a system Σ , when the system deviates from Σ by a small perturbation or fluctuation, there will be a resuming force to restore this system to return to the stable state Σ . Second, we know that a stable equilibrium state of a thermal system

must be the minimal value point of the thermodynamic potential.

By the mathematical characterization of gradient systems and the le Châtelier principle, for a system with thermodynamic potential $\mathcal{H}(u, \lambda)$, the governing equations are essentially determined by the functional $\mathcal{H}(u, \lambda)$. When the order parameters (u_1, \dots, u_m) are nonconserved variables, i.e., the integers

$$\int_{\Omega} u_i(x, t) dx = a_i(t) \neq \text{constant}.$$

then the time-dependent equations are given by

$$\begin{aligned} \frac{\partial u_i}{\partial t} &= -\beta_i \frac{\delta}{\delta u_i} \mathcal{H}(u, \lambda) + \Phi_i(u, \nabla u, \lambda), \\ \frac{\partial u}{\partial n} \Big|_{\partial\Omega} &= 0 \quad (\text{or } u|_{\partial\Omega} = 0), \\ u(x, 0) &= \varphi(x), \end{aligned} \quad (\text{II.7})$$

for any $1 \leq i \leq m$, where $\delta/\delta u_i$ are the variational derivative, $\beta_i > 0$ and Φ_i satisfy

$$\int_{\Omega} \sum_i \Phi_i \frac{\delta}{\delta u_i} \mathcal{H}(u, \lambda) dx = 0. \quad (\text{II.8})$$

The condition (II.8) is required by the Le Châtelier principle. In the concrete problem, the terms Φ_i can be determined by physical laws and (II.8).

When the order parameters are the number density and the system has no material exchange with the external, then u_j ($1 \leq j \leq m$) are conserved, i.e.,

$$\int_{\Omega} u_j(x, t) dx = \text{constant}. \quad (\text{II.9})$$

This conservation law requires a continuous equation

$$\frac{\partial u_j}{\partial t} = -\nabla \cdot J_j(u, \lambda), \quad (\text{II.10})$$

where $J_j(u, \lambda)$ is the flux of component u_j . In addition, J_j satisfy

$$J_j = -k_j \nabla (\mu_j - \sum_{i \neq j} \mu_i), \quad (\text{II.11})$$

where μ_i is the chemical potential of component u_i ,

$$\mu_j - \sum_{i \neq j} \mu_i = \frac{\delta}{\delta u_j} \mathcal{H}(u, \lambda) - \phi_j(u, \nabla u, \lambda), \quad (\text{II.12})$$

and $\phi_j(u, \lambda)$ is a function depending on the other components u_i ($i \neq j$). When $m = 1$, i.e., the system consists of two components A and B , this term $\phi_j = 0$. Thus, from (II.10)-(II.12) we obtain the dynamical equations as follows

$$\begin{aligned} \frac{\partial u_j}{\partial t} &= \beta_j \Delta \left[\frac{\delta}{\delta u_j} \mathcal{H}(u, \lambda) - \phi_j(u, \nabla u, \lambda) \right], \\ \frac{\partial u}{\partial n} \Big|_{\partial\Omega} &= 0, \quad \frac{\partial \Delta u}{\partial n} \Big|_{\partial\Omega} = 0, \\ u(x, 0) &= \varphi(x), \end{aligned} \quad (\text{II.13})$$

for $1 \leq j \leq m$, where $\beta_j > 0$ are constants, ϕ_j satisfy

$$\int_{\Omega} \sum_j \Delta \phi_j \cdot \frac{\delta}{\delta u_j} \mathcal{H}(u, \lambda) dx = 0. \quad (\text{II.14})$$

If the order parameters (u_1, \dots, u_k) are coupled to the conserved variables (u_{k+1}, \dots, u_m) , then the dynamical equations are

$$\begin{aligned} \frac{\partial u_i}{\partial t} &= -\beta_i \frac{\delta}{\delta u_i} \mathcal{H}(u, \lambda) + \Phi_i(u, \nabla u, \lambda), \\ \frac{\partial u_j}{\partial t} &= \beta_j \Delta \left[\frac{\delta}{\delta u_j} \mathcal{H}(u, \lambda) - \phi_j(u, \nabla u, \lambda) \right], \\ \frac{\partial u_i}{\partial n} \Big|_{\partial \Omega} &= 0 \quad (\text{or } u_i \Big|_{\partial \Omega} = 0), \\ \frac{\partial u_j}{\partial n} \Big|_{\partial \Omega} &= 0, \quad \frac{\partial \Delta u_j}{\partial n} \Big|_{\partial \Omega} = 0, \\ u(x, 0) &= \varphi(x). \end{aligned} \quad (\text{II.15})$$

for $1 \leq i \leq k$ and $k+1 \leq j \leq m$.

The model (II.15) gives a general form of the governing equations to thermodynamic phase transitions. Hence, the dynamics of equilibrium phase transition in statistic physics is based on the new Ginzburg-Landau formulation (II.15).

Physically, the initial value condition $u(0) = \varphi$ in (II.15) stands for the fluctuation of system or perturbation from the external. Hence, φ is generally small. However, we can not exclude the possibility of a bigger noise φ .

From conditions (II.8) and (II.14) it follows that a steady state solution u_0 of (II.15) satisfies

$$\begin{aligned} \Phi_i(u_0, \nabla u_0, \lambda) &= 0 \quad \forall 1 \leq i \leq k, \\ \Delta \phi_j(u_0, \nabla u_0, \lambda) &= 0 \quad \forall k+1 \leq j \leq m. \end{aligned} \quad (\text{II.16})$$

Hence a stable equilibrium state must reach the minimal value of thermodynamic potential. In fact, u_0 fulfills

$$\begin{aligned} \beta_i \frac{\delta}{\delta u_i} \mathcal{H}(u_0, \lambda) - \Phi_i(u_0, \nabla u_0, \lambda) &= 0, \\ \beta_j \Delta \frac{\delta}{\delta u_j} \mathcal{H}(u_0, \lambda) - \Delta \phi_j(u_0, \nabla u_0, \lambda) &= 0, \\ \frac{\partial u_i}{\partial n} \Big|_{\partial \Omega} &= 0 \quad (\text{or } u_i \Big|_{\partial \Omega} = 0), \\ \frac{\partial u_j}{\partial n} \Big|_{\partial \Omega} &= 0, \quad \frac{\partial \Delta u_j}{\partial n} \Big|_{\partial \Omega} = 0, \end{aligned} \quad (\text{II.17})$$

for $1 \leq i \leq k$ and $k+1 \leq j \leq m$. Multiplying $\Phi_i(u_0, \nabla u_0, \lambda)$ and $\phi_j(u_0, \nabla u_0, \lambda)$ on the first and the second equations of (II.17) respectively, and integrating them, then we infer from (II.8) and (II.14) that

$$\begin{aligned} \int_{\Omega} \sum_i \Phi_i^2(u_0, \nabla u_0, \lambda) dx &= 0, \\ \int_{\Omega} \sum_j |\nabla \phi_j(u_0, \nabla u_0, \lambda)|^2 dx &= 0, \end{aligned}$$

which imply that (II.16) holds true.

III. TIME-DEPENDENT MODEL FOR PVT SYSTEMS

In this section, we use the general principles derived in the last section to derive a time-dependent Ginzburg-Landau model for PVT systems, which will be used to carry out dynamic transition analysis and physical predictions in the next section.

A. van der Waals equations and Gibbs energy

The classical and the simplest equation of state which can exhibit many of the essential features of the gas-liquid phase transition is the van der Waals equation. It reads

$$v^3 - \left(b + \frac{RT}{p}\right) v^2 + \frac{a}{p} v - \frac{ab}{p} = 0, \quad (\text{III.1})$$

where v is the molar volume, p is the pressure, T is the temperature, R is the universal gas constant, b is the revised constant of inherent volume, and a is the revised constant of attractive force between molecules. If we adopt the molar density $\rho = 1/v$ to replace v in (III.1), then the van der Waals equation becomes

$$-(bp + RT)\rho + a\rho^2 - ab\rho^3 + p = 0. \quad (\text{III.2})$$

Now, we shall apply thermodynamic potentials to investigate the phase transitions of PVT systems, and we shall see later that the van der Waals equation can be derived as a Euler-Lagrange equation for the minimizers of the Gibbs free energy for PVT systems at gaseous states.

Consider an isothermal-isopiestic process. The thermodynamic potential is taken to be the Gibbs free energy. In this case, the order parameters are the molar density ρ and the entropy S , and the control parameters are the pressure p and temperature T . The general form of the Gibbs free energy for PVT systems is given as

$$\begin{aligned} G(\rho, S, T, p) &= \int_{\Omega} \left[\frac{1}{2} \mu_1 |\nabla \rho|^2 + \frac{1}{2} \mu_2 |\nabla S|^2 + g(\rho, S, T, p) \right. \\ &\quad \left. - ST - \alpha(\rho, T, p)\rho \right] dx, \end{aligned} \quad (\text{III.3})$$

where g and α are differentiable with respect to ρ and S , $\Omega \subset \mathbb{R}^3$ is the container, and αp is the mechanical coupling term in the Gibbs free energy, which can be expressed by

$$\alpha(\rho, T, p)p = \rho p - \frac{1}{2} b \rho^2 p, \quad (\text{III.4})$$

where $b = b(T, p)$ depends continuously on T and p .

Based on both the physical and mathematical considerations, we take the Taylor expansion of $g(\rho, S, T, p)$ on ρ and S as follows

$$g = \frac{1}{2} \alpha_1 \rho^2 + \frac{1}{2} \beta_2^S + \beta_2 S \rho^2 - \frac{1}{3} \alpha_2 \rho^3 + \frac{1}{4} \alpha_3 \rho^4, \quad (\text{III.5})$$

where α_i ($1 \leq i \leq 3$), β_1 and β_2 depend continuously on T and p , and

$$\begin{aligned}\alpha_i &= \alpha_i(T, p) > 0 \quad i = 2, 3, \\ \beta_1 &= \beta_1(T, p) > 0.\end{aligned}\quad (\text{III.6})$$

B. Dynamical equations for PVT systems

In a *PVT* system, the order parameter is $u = (\rho, S)$,

$$\rho = \rho_1 - \rho_0, \quad S = S_1 - S_0,$$

where ρ_i and S_i ($i = 0, 1$) represent the density and entropy, ρ_0, S_0 are reference points. Hence the conjugate variables of ρ and S are the pressure p and the temperature T . Thus, by the standard model (II.7), we derive from (III.3)-(III.5) the following general form of the time-dependent equations governing a *PVT* system:

$$\begin{aligned}\frac{\partial \rho}{\partial t} &= \mu_1 \Delta \rho - (\alpha_1 + bp)\rho + \alpha_2 \rho^2 \\ &\quad - \alpha_3 \rho^3 - 2\beta_2 \rho S + p, \\ \frac{\partial S}{\partial t} &= \mu_2 \Delta S - \beta_1 S - \beta_2 \rho^2 + T.\end{aligned}\quad (\text{III.7})$$

Although the domain Ω depends on T and p , we can still take the Neumann boundary condition

$$\left. \frac{\partial \rho}{\partial n} \right|_{\partial \Omega} = 0, \quad \left. \frac{\partial S}{\partial n} \right|_{\partial \Omega} = 0. \quad (\text{III.8})$$

An important special case for *PVT* systems is that the pressure and temperature functions are homogeneous in Ω . Thus we can assume that ρ and S are independent of $x \in \Omega$, and the free energy (III.3) with (III.4) and (III.5) can be expressed as

$$\begin{aligned}G(\rho, S, T, p) &= \frac{1}{2}\alpha_1 \rho^2 + \frac{1}{2}\beta_1 S^2 + \beta_2 S \rho^2 - \frac{1}{3}\alpha_2 \rho^3 \\ &\quad + \frac{1}{4}\alpha_3 \rho^4 + \frac{1}{2}b \rho^2 p - \rho p - ST.\end{aligned}\quad (\text{III.9})$$

From (III.9) we get the dynamical equations as

$$\begin{aligned}\frac{d\rho}{dt} &= -(\alpha_1 + bp)\rho + \alpha_2 \rho^2 \\ &\quad - \alpha_3 \rho^3 - 2\beta_2 S \rho + p, \\ \frac{dS}{dt} &= -\beta_1 S - \beta_2 \rho^2 + T.\end{aligned}\quad (\text{III.10})$$

Because $\beta_1 > 0$ for all T and p , we can replace the second equation of (III.10) by

$$S = \beta_1^{-1}(T - \beta_2 \rho^2). \quad (\text{III.11})$$

Then, (III.10) are equivalent to the following equation

$$\begin{aligned}\frac{d\rho}{dt} &= -(\alpha_1 + bp + 2\beta_1^{-1}\beta_2 T)\rho + \alpha_2 \rho^2 \\ &\quad - (\alpha_3 - 2\beta_2^2 \beta_1^{-1})\rho^3 + p.\end{aligned}\quad (\text{III.12})$$

It is clear that if $\alpha_1 = 0, 2\beta_1^{-1}\beta_2 = R, \alpha_2 = a, (\alpha_3 - 2\beta_2^2 \beta_1^{-1}) = ab$, then the steady state equation of (III.12) is referred to the van der Waals equation.

IV. PHASE TRANSITION DYNAMICS FOR PVT SYSTEMS

In this section we use (III.12) to discuss dynamical properties of transitions for *PVT* systems, and remark that similar results can also derived using the more general form of the time-dependent model (III.7).

Let ρ_0 be a steady state solution of (III.12). We take the transformation

$$\rho = \rho_0 + \rho'.$$

Then equation (III.12) becomes (drop the prime)

$$\frac{d\rho}{dt} = \lambda \rho + a_2 \rho^2 - a_3 \rho^3. \quad (\text{IV.1})$$

where

$$\begin{aligned}\lambda &= 2\alpha_2 \rho_0 - 3a_3 \rho_0^2 - \alpha_1 - bp - 2\beta_2 \beta_1^{-1} T, \\ a_2 &= \alpha_2 - 3a_3 \rho_0, \\ a_3 &= \alpha_3 - 2\beta_2^2 \beta_1^{-1}.\end{aligned}$$

In the *PT*-plane, near a non-triple point $A = (T^*, p^*)$ (see Figure 1), the critical parameter equation

$$\lambda = \lambda(T, p) = 0 \quad \text{in} \quad |T - T^*| < \delta, \quad |p - p^*| < \delta$$

for some $\delta > 0$, defines a continuous function $T = \phi(p)$, such that

$$\lambda \begin{cases} < 0 & \text{if } T > \phi(p), \\ = 0 & \text{if } T = \phi(p), \\ > 0 & \text{if } T < \phi(p). \end{cases} \quad (\text{IV.2})$$

The main result in this section is the following dynamic transition theorem for *PVT* systems.

Theorem IV.1 *Let $T_0 = \phi(p_0)$ and $a_3 > 0$. Then the system (IV.1) has a transition at $(T, p) = (T_0, p_0)$, and the following assertions hold true:*

1. *If the coefficient $a_2 = a_2(T, p)$ in (IV.1) is zero at (T_0, p_0) , i.e., $a_2(T_0, p_0) = 0$, then the transition is of Type-I, as schematically shown in Figure 3 (a) and (b).*
2. *If $a_2(T_0, p_0) \neq 0$, then the transition is of Type-III (i.e., the mixed type), and the following assertions hold true:*

(a) *There are two transition solutions near (T_0, p_0) as*

$$\rho^\pm(T, p) = \frac{1}{2a_3} \left(a_2 \pm \sqrt{a_2^2 + 4a_3 \lambda} \right). \quad (\text{IV.3})$$

(b) *There is a saddle-node bifurcation at (T_1, p_1) , where $T_1 > T_0$ and $p_1 < p_0$ if $\phi'(p_0) > 0$, and $p_0 > p_1$ if $\phi'(p_0) < 0$.*

- (c) For $\phi'(p_0) > 0$, when $a_2(T_0, p_0) > 0$ the transition diagrams are illustrated by Figure 4 (a)-(b), where ρ^+ is stable for all (T, p) near (T_0, p_0) , and $\rho = 0$ is stable, ρ^- a saddle for $T_0 < T < T_1$ and $p_1 < p < p_0$, and ρ^- is stable, $\rho = 0$ a saddle for $T < T_0, p > p_0$;
- (d) When $a_2(T_0, p_0) < 0$, the transition diagrams are illustrated by Figure 5(a)-(b), where ρ^- is stable for all (T, p) near (T_0, p_0) , and $\rho = 0$ is stable, ρ^+ a saddle for $T_0 < T < T_1, p_1 < p < p_0$, and ρ^+ is stable, $\rho = 0$ a saddle for $T < T_0, p_0 < p$.

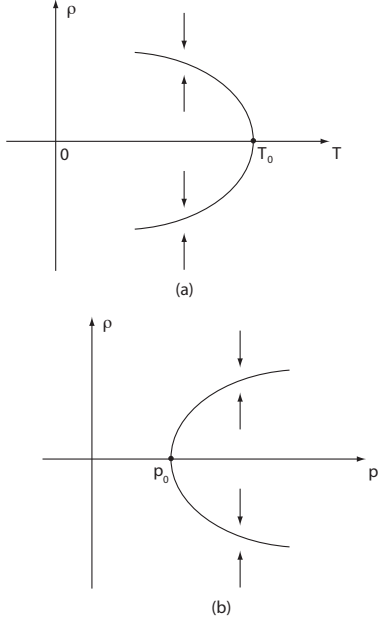


FIG. 3: Continuous transition for the case where $\phi'(p_0) > 0$

Proof. By (IV.1), the theorem follows from the transition theorems (Theorems A.2 and A.3) and the singularity separation theorem (Theorem A.4). We omit the detailed routine analysis. ■

V. PHYSICAL CONCLUSIONS AND PREDICTIONS

To discuss the physical significance of Theorem IV.1, we recall the classical pV -phase diagram given by Figure 2. We take $\rho = 1/V$ to replace volume V , then the gas-liquid coexistence curve in the ρ - P plane is illustrated by Figure 6.

According to the physical experiments, in the gas-liquid coexistence region in the ρ - p phase diagram, there exist metastable states. Mathematically speaking, the metastable states are the attractors which have a small basin of attraction. In Figure 6, the dashed lines aa' and bb' represent the metastable states, and the points

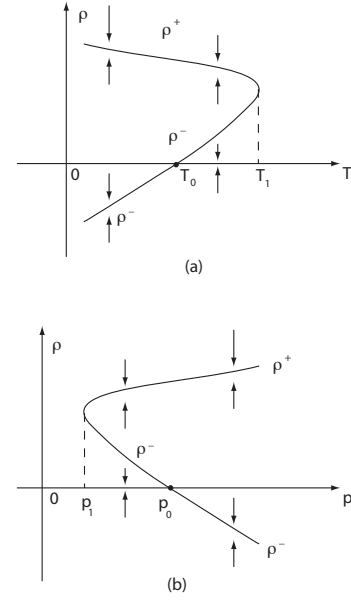


FIG. 4: Type-III (mixed) transition for $a_2 > 0$.

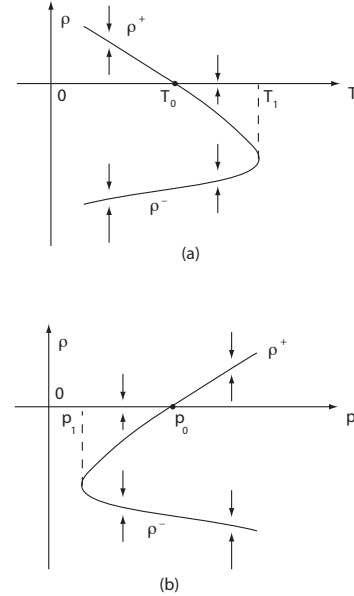


FIG. 5: Type-III (mixed) transition for $a_2 < 0$.

in aa' correspond to super-heated liquid, the points in bb' correspond to super-cooled gas. The ρ - p phase diagram shows that along the isothermal line $T > T_C$ where $C = (T_C, P_C)$ is the Andrews critical point, when the pressure p increases, the density ρ varies continuously from gaseous to liquid states. However along the isothermal line $T < T_C$ when the pressure p increases to p_0 the density ρ will undergo an abrupt change, and a transition from gaseous state a to a liquid state b accom-

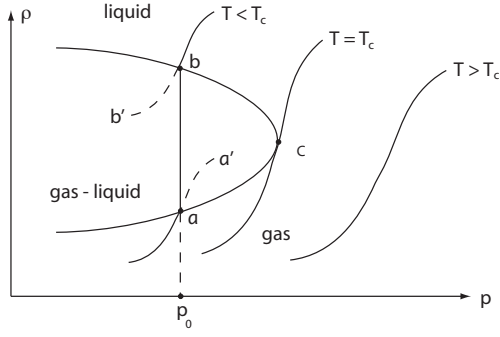


FIG. 6: The gas-liquid coexistence curve in $\rho-p$ plane: point C is the Andrews critical point, the dashed lines aa' and bb' stand for the metastable states.

panied with an isothermal exothermal process to occur. Likewise, such processes also occur in the gas-solid and liquid-solid transitions.

We now return to discuss Theorem IV.1. The steady state solution $\rho_0 = \rho_0(T, p)$ of (III.12) can be taken to represent a desired state in investigating different transition situation. For example, for studying the gas-liquid transition we can take ρ_0 as the gas density near the transition temperature and pressure, and for the liquid-solid transition we take ρ_0 as the liquid density, i.e., the lower state density. For convenience, in the following we always consider the gas-liquid transition, and take ρ_0 as the gas density.

Let $T_0 = \phi(p_0)$, and $\phi'(p_0) > 0$. Then Theorem IV.1 implies the following physical conclusions:

FIRST, near (T_0, p_0) , there are three stable equilibrium states of (III.12) for each of the three cases: $a_2 > 0$, $a_2 = 0$, or $a_2 < 0$:

a) If $a_2 < 0$, they are

$$\begin{aligned} \varphi^+ &= \rho_0 + \rho^+ & \text{for } |T - T_0| < \delta \text{ \& } |p - p_0| < \delta, \\ \varphi^0 &= \rho_0 & \text{for } T_0 < T \text{ or } p < p_0, \\ \varphi^- &= \rho_0 + \rho^- & \text{for } T < T_0 \text{ \& } p > p_0; \end{aligned} \quad (\text{V.1})$$

b) If $a_2 = 0$, they are

$$\begin{aligned} \varphi^\pm &= \rho_0 + \rho^\pm & \text{for } T < T_0 \text{ \& } p > p_0, \\ \varphi^0 &= \rho_0 & \text{for } T > T_0 \text{ or } p < p_0, \end{aligned} \quad (\text{V.2})$$

where $\rho^\pm = \pm\sqrt{\lambda/a_3}$;

c) If $a_2 < 0$, they are

$$\begin{aligned} \varphi^+ &= \rho_0 + \rho^+ & \text{for } T < T_0 \text{ \& } p > p_0, \\ \varphi^0 &= \rho_0 & \text{for } T > T_0 \text{ or } p < p_0, \\ \varphi^- &= \rho_0 + \rho^- & \text{for } |T - T_0| < \delta \text{ \& } |p - p_0| < \delta. \end{aligned} \quad (\text{V.3})$$

Here the state φ^+ represents the liquid density, φ^0 the real gas density, and φ^- the underlying state density.

SECOND, putting $S = \beta_1^{-1}(T - \beta_2\rho^2)$ into (III.9), the free energy becomes

$$\begin{aligned} G(\rho, T, p) &= -\frac{1}{2}\beta_1^{-1}T^2 + \frac{1}{2}(\alpha_1 + bp + 2\beta_1^{-1}\beta_2T)\rho^2 \\ &\quad -\frac{1}{3}\alpha_2\rho^3 + \frac{1}{4}(\alpha_3 - 2\beta_2^2\beta_1^{-1})\rho^4 - p\rho. \end{aligned}$$

The values of G at equilibrium states of (IV.1) are given by

$$\begin{aligned} G(\rho_0 + \rho^\pm) &= G(\rho_0) - \frac{\lambda}{2}(\rho^\pm)^2 - \frac{a_2}{3}(\rho^\pm)^3 + \frac{a_3}{4}(\rho^\pm)^4 \\ &= G(\rho_0) - \frac{\lambda}{4}(\rho^\pm)^2 - \frac{a_2}{12}(\rho^\pm)^3. \end{aligned} \quad (\text{V.4})$$

By $\lambda = 0$ at (T_0, p_0) , it follows from (V.1)-(V.4) that for (T, p) near (T_0, p_0) we have

$$\begin{aligned} G(\varphi^+) &< G(\varphi^0) < G(\varphi^-) & \text{for } a_2 > 0, \\ G(\varphi^+) &= G(\varphi^-) < G(\varphi^0) & \text{for } a_2 = 0, \\ G(\varphi^-) &< G(\varphi^0) < G(\varphi^+) & \text{for } a_2 < 0. \end{aligned} \quad (\text{V.5})$$

THIRD, according to Theorem IV.1 and the transition diagrams (Figures 3-5), there are two types of transition behaviors characterized by some functions $\Phi = \rho(T, p)$ near $(T, p) = (T_0, p_0)$, which are called the transition functions. Here, for simplicity we fixed $p = p_0$ and consider $\Phi = \rho(T)$ as function of T .

If $a_2 > 0$, the transition functions are

$$\begin{aligned} \Phi^+(T) &= \begin{cases} \rho_0(T) & \text{for } T > T^*, \\ \rho_0(T) + \rho^+(T) & \text{for } T < T^*, \end{cases} \\ \Phi^-(T) &= \begin{cases} \rho_0(T) & \text{for } T \geq T_0, \\ \rho_0(T) + \rho^- & \text{for } T < T_0, \end{cases} \end{aligned}$$

for some $T_0 \leq T^* < T_1$. $\Phi^+(T)$ has a finite jump at $T = T^*$ as shown in Figure 7(a), and $\Phi^-(T)$ is continuous, but has a discontinuous derivative at $T = T_0$; see Figure 7(b).

If $a_2 = 0$, the functions are

$$\begin{aligned} \Phi^+(T) &= \begin{cases} \rho_0(T) & \text{for } T \geq T_0, \\ \rho_0(T) + \rho^+(T) & \text{for } T < T_0, \end{cases} \\ \Phi^-(T) &= \begin{cases} \rho_0(T) & \text{for } T \geq T_0, \\ \rho_0(T) + \rho^-(T) & \text{for } T < T_0, \end{cases} \end{aligned}$$

and Φ^+ and Φ^- are continuous with discontinuous derivatives at $T = T_0$; see Figure 8(a) and (b).

If $a_2 < 0$, the functions are

$$\begin{aligned} \Phi^+(T) &= \begin{cases} \rho_0(T) & \text{for } T \geq T_0, \\ \rho_0(T) + \rho^+(T) & \text{for } T < T_0, \end{cases} \\ \Phi^-(T) &= \begin{cases} \rho_0(T) & \text{for } T > T^*, \\ \rho_0(T) + \rho^-(T) & \text{for } T < T^*, \end{cases} \end{aligned}$$

for some $T_0 \leq T^* < T_1$, Φ^+ is continuous with a discontinuous derivative at $T = T_0$ as shown in Figure 9(a), and Φ^- is discontinuous at $T = T^*$ as shown in Figure 9(b).

FOURTH, based on physical facts, near the gas-liquid transition point (T_0, p_0) the density ρ is a decreasing function of T , therefore the transition process Φ^+ is realistic, and Φ^- is unrealistic. From the transition function $\Phi^+(T)$, the gas-liquid transition can be well understood.

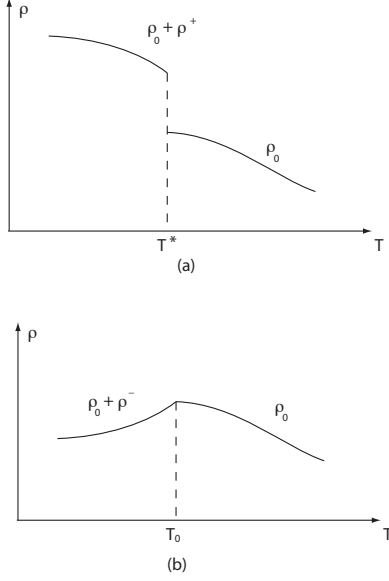


FIG. 7: The transition functions for $a_2 > 0$: (a) the curve of $\rho = \Phi^+$, (b) the curve of $\rho = \Phi^-$.

FIFTH, we now explain the gas-liquid transition by using the transition function $\Phi^+(T)$. Let the two curves

$$\lambda = \lambda(T, p) = 0 \quad \text{and} \quad a_2 = a_2(T, p) = 0 \quad (\text{V.6})$$

intersect at $C = (T_C, p_C)$ in PT -plane (see Figure 10), and the curve segment AB of $\lambda = 0$ is divided into two parts AC and CB by the point C such that

$$\begin{aligned} a_2(T, p) &> 0 & \text{for } (T, p) \in AC, \\ a_2(T, p) &< 0 & \text{for } (T, p) \in CB. \end{aligned}$$

We shall see that the point $C = (T_C, p_C)$ is the Andrews critical point, and the curve segment AC is the gas-liquid coexistence curve, as shown in Figure 1.

In fact, when $(T_0, p_0) \in AC$, $a_2(T_0, p_0) > 0$ and the transition function $\Phi^+(T)$ has a jump at $T = T^*$ (see Figure 6(a)):

$$\rho_0 \rightarrow \rho_0 + \rho^+, \quad \rho^+ \simeq \frac{a_2}{a_3} > 0.$$

Hence the system undergoes a transition from a gaseous state to a liquid state with an abrupt change in density.

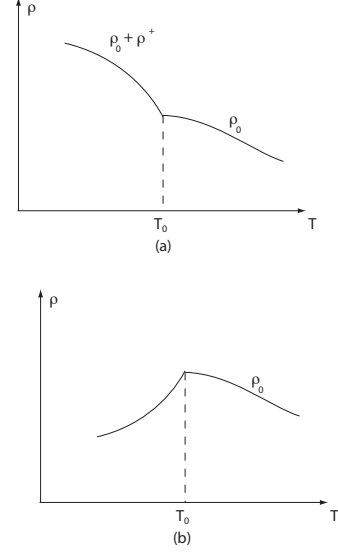


FIG. 8: The transition functions for $a_2 = 0$: (a) the curve of $\rho = \Phi^+$, (b) the curve of $\rho = \Phi^-$.

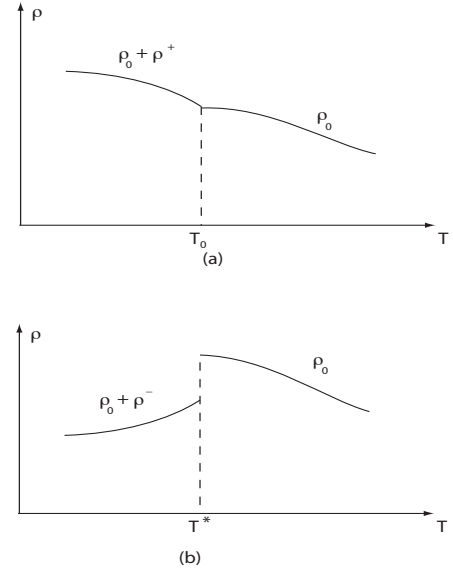


FIG. 9: The transition functions for $a_2 < 0$: (a) the curve of $\rho = \Phi^+$, (b) the curve of $\rho = \Phi^-$.

On the other hand, by (V.5) there is an energy gap between the gaseous and liquid states:

$$\Delta E = G(\rho_0 + \rho^+) - G(\rho_0) < 0 \quad \text{at } T = T^*.$$

This energy gap $|\Delta E|$ stands for a latent heat, and $\Delta E < 0$ shows that the transition from a gaseous state to a liquid state is an isothermal exothermal process, and from a liquid state to gaseous state is an isothermal endothermal process.

When $(T_0, p_0) = (T_C, p_C)$, $a_2(T_C, p_C) = 0$ and the

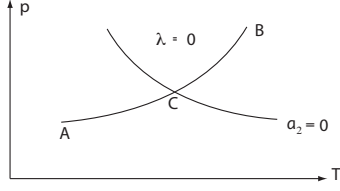


FIG. 10:

transition function $\Phi^+(T)$ is continuous as shown in Figure 8(a). Near $T = T_C$,

$$\Phi^+(T) = \rho_0(T) + \sqrt{\lambda/a_3} \quad \text{for } T < T_C.$$

By the Landau mean field theory, we have

$$\lambda(T) = \alpha(T_C - T) \quad (\alpha > 0 \text{ a constant}). \quad (\text{V.7})$$

Thus we infer from (V.4) and (V.7) that

$$G(\Phi^+(T)) = G(\rho_0) - \frac{\alpha^2}{4a_3}(T - T_C)^2 \quad \text{for } T < T_C.$$

The difference of the heat capacity at $T = T_C$ is

$$\Delta C = -T_C \frac{\partial^2}{\partial T^2} (G(\Phi^+(T_C + 0)) - G(\rho_0)) = \frac{\alpha^2}{2a_3} T_C > 0.$$

Namely the heat capacity has a finite jump at $T = T_C$, therefore the transition at $T = T_C$ is of the second order.

When $(T_0, p_0) \in CB$, $a_2(T_0, p_0) < 0$ and the transition function $\Phi^+(T)$ is continuous as shown in Figure 9(a). Near $T = T_0$,

$$\Phi^+(T) = \rho_0(T) + \frac{1}{|a_2|} \lambda(T) + o(|\lambda|) \quad T \leq T_0.$$

Notice that (IV.3) implies that

$$\rho^+ = \frac{\lambda}{a_2} + o(|\lambda|).$$

Then we deduce from (V.4) and (V.7) that if $T > T_0$,

$$G(\Phi^+(T)) = G(\rho_0(T)),$$

and if $T \leq T_0$,

$$G(\Phi^+(T)) = G(\rho_0(T)) - \frac{\alpha^3}{6|a_2|^2}(T_0 - T)^3 + o(|T_0 - T|^3).$$

Namely, the free energy $G(\Phi^+(T))$ is continuously differentiable up to the second order at $T = T_0$, and the transition is of the third order. It implies that as $(T_0, p_0) \in CB$ the Type-I transition at (T_0, p_0) can not

be observed by physical experiments. Therefore we can derive the following physical conclusion:

Physical Conclusion V.1. *The point $C = (T_C, p_C)$ satisfying (V.6) corresponds to the Andrews critical point, at which the gas-liquid transition is of the second order. In addition, when $\lambda(T_0, p_0) = 0, a_2(T_0, p_0) > 0$, the gas-liquid transition at (T_0, p_0) is of the first order accompanied with a latent heat to occur, and when $\lambda(T_0, p_0) = 0, a_2(T_0, p_0) < 0$, the transition at (T_0, p_0) is of the third order.*

SIXTH, as $\lambda(T_0, p_0) = 0$ and $a_2(T_0, p_0) > 0$, the gas-liquid transition point (T^*, p^*) is in the range $T_0 \leq T^* < T_1$ and $p_1 < p^* \leq p_0$; see Figure 4(a)-(b). In fact, in the region $T_0 \leq T < T_1$ and $p_1 < p < p_0$, the two stable states $\varphi^0 = \rho_0(T, p)$ and $\varphi^+ = \rho_0(T, p) + \rho^+(T, p)$ are attractors, each possessing a small basin of attraction. Therefore they correspond to metastable states, and φ^0 can be considered as a super cooled gas, while φ^+ can be considered as a super heated liquid.

FINALLY, likewise, we can also discuss the gas-solid and liquid-solid transitions, and derive the following physical conclusion:

Physical Conclusion V.2. *In the gas-solid and liquid-solid transitions, there also exist metastable states. For the gas-solid case, the metastable states correspond to the superheated solid and supercooled liquid, and for the liquid-solid case, the metastable states correspond to the superheated solid and supercooled liquid.*

APPENDIX A: RECAPITULATION OF THE DYNAMIC TRANSITION THEORY OF NONLINEAR SYSTEMS

In this appendix we recall some basic elements of the dynamic transition theory developed by the authors [1, 2], which are used to carry out the dynamic transition analysis for the PVT systems in this article.

Let X and X_1 be two Banach spaces, and $X_1 \subset X$ a compact and dense inclusion. In this chapter, we always consider the following nonlinear evolution equations

$$\begin{aligned} \frac{du}{dt} &= L_\lambda u + G(u, \lambda), \\ u(0) &= \varphi, \end{aligned} \quad (\text{A.1})$$

where $u : [0, \infty) \rightarrow X$ is unknown function, and $\lambda \in \mathbb{R}^1$ is the system parameter.

Assume that $L_\lambda : X_1 \rightarrow X$ is a parameterized linear completely continuous field depending contiguously on $\lambda \in \mathbb{R}^1$, which satisfies

$$\begin{aligned} L_\lambda &= -A + B_\lambda && \text{a sectorial operator,} \\ A : X_1 &\rightarrow X && \text{a linear homeomorphism,} \\ B_\lambda : X_1 &\rightarrow X && \text{a linear compact operator.} \end{aligned} \quad (\text{A.2})$$

In this case, we can define the fractional order spaces X_σ for $\sigma \in \mathbb{R}^1$. Then we also assume that $G(\cdot, \lambda) : X_\alpha \rightarrow X$ is C^r ($r \geq 1$) bounded mapping for some $0 \leq \alpha < 1$, depending continuously on $\lambda \in \mathbb{R}^1$, and

$$G(u, \lambda) = o(\|u\|_{X_\alpha}), \quad \forall \lambda \in \mathbb{R}^1. \quad (\text{A.3})$$

Hereafter we always assume the conditions (A.2) and (A.3), which represent that the system (A.1) has a dissipative structure.

In the following we introduce the definition of transitions for (A.1).

Definition A.1 *We say that the system (A.1) has a transition of equilibrium from $(u, \lambda) = (0, \lambda_0)$ on $\lambda > \lambda_0$ (or $\lambda < \lambda_0$) if the following two conditions are satisfied:*

- (1) *when $\lambda < \lambda_0$ (or $\lambda > \lambda_0$), $u = 0$ is locally asymptotically stable for (A.1); and*
- (2) *when $\lambda > \lambda_0$ (or $\lambda < \lambda_0$), there exists a neighborhood $U \subset X$ of $u = 0$ independent of λ , such that for any $\varphi \in U \setminus \Gamma_\lambda$ the solution $u_\lambda(t, \varphi)$ of (A.1) satisfies that*

$$\begin{aligned} \limsup_{t \rightarrow \infty} \|u_\lambda(t, \varphi)\|_X &\geq \delta(\lambda) > 0, \\ \lim_{\lambda \rightarrow \lambda_0} \delta(\lambda) &\geq 0, \end{aligned}$$

where Γ_λ is the stable manifold of $u = 0$, with $\text{codim } \Gamma_\lambda \geq 1$ in X for $\lambda > \lambda_0$ (or $\lambda < \lambda_0$).

Obviously, the attractor bifurcation of (A.1) is a type of transition. However, bifurcation and transition are two different, but related concepts. Definition A.1 defines the transition of (A.1) from a stable equilibrium point to other states (not necessary equilibrium state). In general, we can define transitions from one attractor to another as follows.

Definition A.2 *Let $\Sigma_\lambda \subset X$ be an invariant set of (A.1). We say that (A.1) has a transition of states from $(\Sigma_{\lambda_0}, \lambda_0)$ on $\lambda > \lambda_0$ (or $\lambda < \lambda_0$) if the following conditions are satisfied:*

- (1) *when $\lambda < \lambda_0$ (or $\lambda > \lambda_0$), Σ_λ is a local minimal attractor, and*
- (2) *when $\lambda > \lambda_0$ (or $\lambda < \lambda_0$), there exists a neighborhood $U \subset X$ of Σ_λ independent of λ such that for any $\varphi \in U \setminus (\Gamma_\lambda \cup \Sigma_\lambda)$, the solution $u(t, \varphi)$ of (A.1) satisfies that*

$$\begin{aligned} \limsup_{t \rightarrow \infty} \text{dist}(u(t, \varphi), \Sigma_\lambda) &\geq \delta(\lambda) > 0, \\ \lim_{\lambda \rightarrow \lambda_0} \delta(\lambda) &= \delta \geq 0, \end{aligned}$$

where Γ_λ is the stable manifolds of Σ_λ with $\text{codim } \Gamma_\lambda \geq 1$.

Let the eigenvalues (counting multiplicity) of L_λ be given by

$$\{\beta_j(\lambda) \in \mathbb{C} \mid j = 1, 2, \dots\}$$

Assume that

$$\text{Re } \beta_i(\lambda) \begin{cases} < 0 & \text{if } \lambda < \lambda_0, \\ = 0 & \text{if } \lambda = \lambda_0, \\ > 0 & \text{if } \lambda > \lambda_0, \end{cases} \quad \forall 1 \leq i \leq m, \quad (\text{A.4})$$

$$\text{Re } \beta_j(\lambda_0) < 0 \quad \forall j \geq m + 1. \quad (\text{A.5})$$

The following theorem is a basic principle of transitions from equilibrium states, which provides sufficient conditions and a basic classification for transitions of nonlinear dissipative systems. This theorem is a direct consequence of the center manifold theorems and the stable manifold theorems; we omit the proof.

Theorem A.1 *Let the conditions (A.4) and (A.5) hold true. Then, the system (A.1) must have a transition from $(u, \lambda) = (0, \lambda_0)$, and there is a neighborhood $U \subset X$ of $u = 0$ such that the transition is one of the following three types:*

- (1) **CONTINUOUS TRANSITION:** *there exists an open and dense set $\tilde{U}_\lambda \subset U$ such that for any $\varphi \in \tilde{U}_\lambda$, the solution $u_\lambda(t, \varphi)$ of (A.1) satisfies*

$$\lim_{\lambda \rightarrow \lambda_0} \limsup_{t \rightarrow \infty} \|u_\lambda(t, \varphi)\|_X = 0.$$

In particular, the attractor bifurcation of (A.1) at $(0, \lambda_0)$ is a continuous transition.

- (2) **JUMP TRANSITION:** *for any $\lambda_0 < \lambda < \lambda_0 + \varepsilon$ with some $\varepsilon > 0$, there is an open and dense set $U_\lambda \subset U$ such that for any $\varphi \in U_\lambda$,*

$$\limsup_{t \rightarrow \infty} \|u_\lambda(t, \varphi)\|_X \geq \delta > 0,$$

where $\delta > 0$ is independent of λ . This type of transition is also called the discontinuous transition.

- (3) **MIXED TRANSITION:** *for any $\lambda_0 < \lambda < \lambda_0 + \varepsilon$ with some $\varepsilon > 0$, U can be decomposed into two open sets U_1^λ and U_2^λ (U_i^λ not necessarily connected):*

$$\bar{U} = \bar{U}_1^\lambda + \bar{U}_2^\lambda, \quad U_1^\lambda \cap U_2^\lambda = \emptyset,$$

such that

$$\begin{aligned} \lim_{\lambda \rightarrow \lambda_0} \limsup_{t \rightarrow \infty} \|u(t, \varphi)\|_X &= 0 & \forall \varphi \in U_1^\lambda, \\ \limsup_{t \rightarrow \infty} \|u(t, \varphi)\|_X &\geq \delta > 0 & \forall \varphi \in U_2^\lambda. \end{aligned}$$

The following theorem provides sufficient conditions for continuous transitions and gives local transition structure.

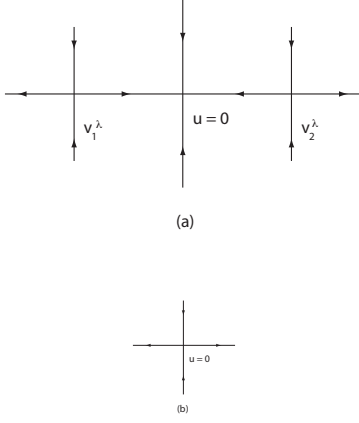


FIG. 11: Topological structure of the jump transition of (A.1) when $k=\text{odd}$ and $\alpha > 0$: (a) $\lambda < \lambda_0$; (b) $\lambda > \lambda_0$. Here the horizontal line represents the center manifold.

We consider the transition of (A.1) from a simple critical eigenvalue. Let the eigenvalues $\beta_j(\lambda)$ of L_λ satisfy

$$\beta_1(\lambda) \begin{cases} < 0 & \text{if } \lambda < \lambda_0, \\ = 0 & \text{if } \lambda = \lambda_0, \\ > 0 & \text{if } \lambda > \lambda_0, \end{cases} \quad (\text{A.6})$$

$$\text{Re}\beta_j(\lambda_0) < 0 \quad \forall j \geq 2,$$

where $\beta_1(\lambda)$ is a real eigenvalue.

Let $e_1(\lambda)$ and $e_1^*(\lambda)$ be the eigenvectors of L_λ and L_λ^* respectively corresponding to $\beta_1(\lambda)$ with

$$L_{\lambda_0} e_1 = 0, \quad L_{\lambda_0}^* e_1^* = 0, \quad \langle e_1, e_1^* \rangle = 1.$$

Let $\Phi(x, \lambda)$ be the center manifold function of (A.1) near $\lambda = \lambda_0$. We assume that

$$\langle G(xe_1 + \Phi(x, \lambda_0), \lambda_0), e_1^* \rangle = \alpha x^k + o(|x|^k), \quad (\text{A.7})$$

where $k \geq 2$ an integer and $\alpha \neq 0$ a real number.

We have the following transition theorems.

Theorem A.2 *Under the conditions (A.6) and (A.7), if $k=\text{odd}$ and $\alpha \neq 0$ in (A.7) then the following assertions hold true:*

- (1) *If $\alpha > 0$, then (A.1) has a jump transition from $(0, \lambda_0)$, and bifurcates on $\lambda < \lambda_0$ to exactly two saddle points v_1^λ and v_2^λ with the Morse index one, as shown in Figure 11.*
- (2) *If $\alpha < 0$, then (A.1) has a continuous transition from $(0, \lambda_0)$, which is an attractor bifurcation as shown in Figure 12.*
- (3) *The bifurcated singular points v_1^λ and v_2^λ in the above cases can be expressed in the following form*

$$v_{1,2}^\lambda = \pm |\beta_1(\lambda)/\alpha|^{1/(k-1)} e_1(\lambda) + o(|\beta_1|^{1/(k-1)}).$$

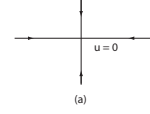


FIG. 12: Topological structure of the continuous transition of (A.1) when $k=\text{odd}$ and $\alpha < 0$: (a) $\lambda \leq \lambda_0$; (b) $\lambda > \lambda_0$.

Theorem A.3 *Under the conditions (A.6) and (A.7), if $k=\text{even}$ and $\alpha \neq 0$, then we have the following assertions:*

1. *(A.1) has a mixed transition from $(0, \lambda_0)$. More precisely, there exists a neighborhood $U \subset X$ of $u = 0$ such that U is separated into two disjoint open sets U_1^λ and U_2^λ by the stable manifold Γ_λ of $u = 0$ satisfying the following properties:*
 - (a) $U = U_1^\lambda + U_2^\lambda + \Gamma_\lambda$,
 - (b) *the transition in U_1^λ is jump, and*
 - (c) *the transition in U_2^λ is continuous. The local transition structure is as shown in Figure 13.*
2. *(A.1) bifurcates in U_2^λ to a unique singular point v^λ on $\lambda > \lambda_0$, which is an attractor such that for any $\varphi \in U_2^\lambda$,*

$$\lim_{t \rightarrow \infty} \|u(t, \varphi) - v^\lambda\|_X = 0,$$

where $u(t, \varphi)$ is the solution of (A.1).

3. *(A.1) bifurcates on $\lambda < \lambda_0$ to a unique saddle point v^λ with the Morse index one.*
4. *The bifurcated singular point v^λ can be expressed as*

$$v^\lambda = -(\beta_1(\lambda)/\alpha)^{1/(k-1)} e_1 + o(|\beta_1|^{1/(k-1)}).$$

We consider the equation (A.1) defined on the Hilbert spaces $X = H, X_1 = H_1$. Let $L_\lambda = -A + \lambda B$. For L_λ and $G(\cdot, \lambda) : H_1 \rightarrow H$, we assume that $A : H_1 \rightarrow H$ is symmetric, and

$$\langle Au, u \rangle_H \geq c \|u\|_{H_{1/2}}^2, \quad (\text{A.8})$$

$$\langle Bu, u \rangle_H \geq c \|u\|_H^2, \quad (\text{A.9})$$

$$\langle Gu, u \rangle_H \leq -c_1 \|u\|_H^p + c_2 \|u\|_H^2, \quad (\text{A.10})$$

where $p > 2, c, c_1, c_2 > 0$ are constants.

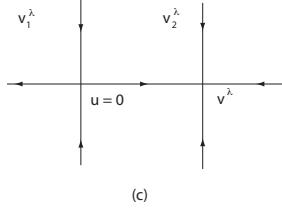
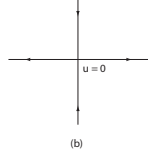
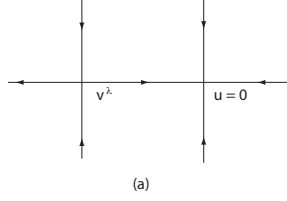


FIG. 13: Topological structure of the mixing transition of (A.1) when $k=\text{even}$ and $\alpha \neq 0$: (a) $\lambda < \lambda_0$; (b) $\lambda = \lambda_0$; (c) $\lambda > \lambda_0$. Here U_1^λ is the unstable domain, and U_2^λ the stable domain.

Theorem A.4 Assume the conditions (A.3), (A.4) and (A.8)-(A.10), then (A.1) has a transition at $(u, \lambda) = (0, \lambda_0)$, and the following assertions hold true:

(1) If $u = 0$ is an even-order nondegenerate singular point of $L_\lambda + G$ at $\lambda = \lambda_0$, then (A.1) has a singular separation of singular points at some $(u_1, \lambda_1) \in H \times (-\infty, \lambda_0)$.

(2) If $m = 1$ and G satisfies (A.7) with $\alpha > 0$ if $k=\text{odd}$ and $\alpha \neq 0$ if $k=\text{even}$, then (A.1) has a saddle-node bifurcation at some singular point (u_1, λ_1) with $\lambda_1 < \lambda_0$.

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